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NACE INTERNATIONAL CORROSION 2011 CONFERENCE & EXPO

LIFETIME PREDICTIONS FOR CARBON STEEL IN NATURAL FRESH WATER

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ABSTRACT

Corrosion rates of carbon steel in Duluth-Superior Harbor (DSH) were measured over a 3-year period using weight loss, pit depth measurements and linear polarization resistance (LPR). Corrosion coupons were placed in racks throughout the harbor and removed periodically for weight loss and pit depth measurements. LPR measurements were made at rack locations. Estimated corrosion rates varied among the techniques and there were no obvious relationships between predicted rates from the three techniques. Penetration rates estimated from pit depths were not linear with time. Pit depth varied among locations, but was consistently deepest during the first year of exposure.

Keywords: carbon steel, pilings, freshwater, polarization resistance, weight loss, profilometry

INTRODUCTION

Carbon steel sheet piling (1.2 cm thick A328[1] cold rolled) used for docks, bridges and bulkheads in the Duluth-Superior Harbor (DSH), MN and WI, is corroding at an accelerated rate.[2,3] Sheet pile structures in DSH that are over thirty years old are either completely or partially perforated by localized corrosion. DSH is located at the extreme western end of Lake Superior and is described as a freshwater estuary.[4] DSH is polymitic, i.e., seiches or free standing wave oscillations are almost always present, suspending particulates into the water column.[5] DSH is icebound from mid-December to mid-April and during that time has a durable, well-defined ice cover.[5] Freeze ice thicknesses in DSH range from 0.5 to 1.4 m in addition to snow ice, stack ice, and ice from wave and splash action along harbor walls.[6]

Corrosion of carbon steel pilings in DSH is a combination of both general and localized attack. Pilings are scoured by ice in late winter and early spring resulting in a general loss of material. Localized corrosion on DSH pilings is characterized by tubercles (Figure 1). Divers report that tubercles are randomly distributed from the waterline to approximately 3 m below the surface.[7] Scott et al.[7] reported that tubercles can be removed by hand and that regrowth occurs. Tubercles vary in diameter

from a few millimeters to several centimeters and when removed, large and often deep pits are exposed. Bushman and Phull[8] determined that stray currents were not the cause of corrosion in DSH. Corrosion is also independent of the type and age of the carbon steel. Recently iron-oxidizing bacteria (IOB) were identified in corrosion products on DSH carbon steel pilings.[9] Ray et al.[9] demonstrated that stalk-forming, IOB colonized the carbon steel sheet pilings and produced tubercles made up of intact and/or partly degraded remains of bacterial cells mixed with amorphous hydrous ferric oxides. The reducing conditions beneath the tubercles caused copper, dissolved in the water, to precipitate. A galvanic couple was established between the copper layer and the iron substratum. The result was aggressive localized corrosion.

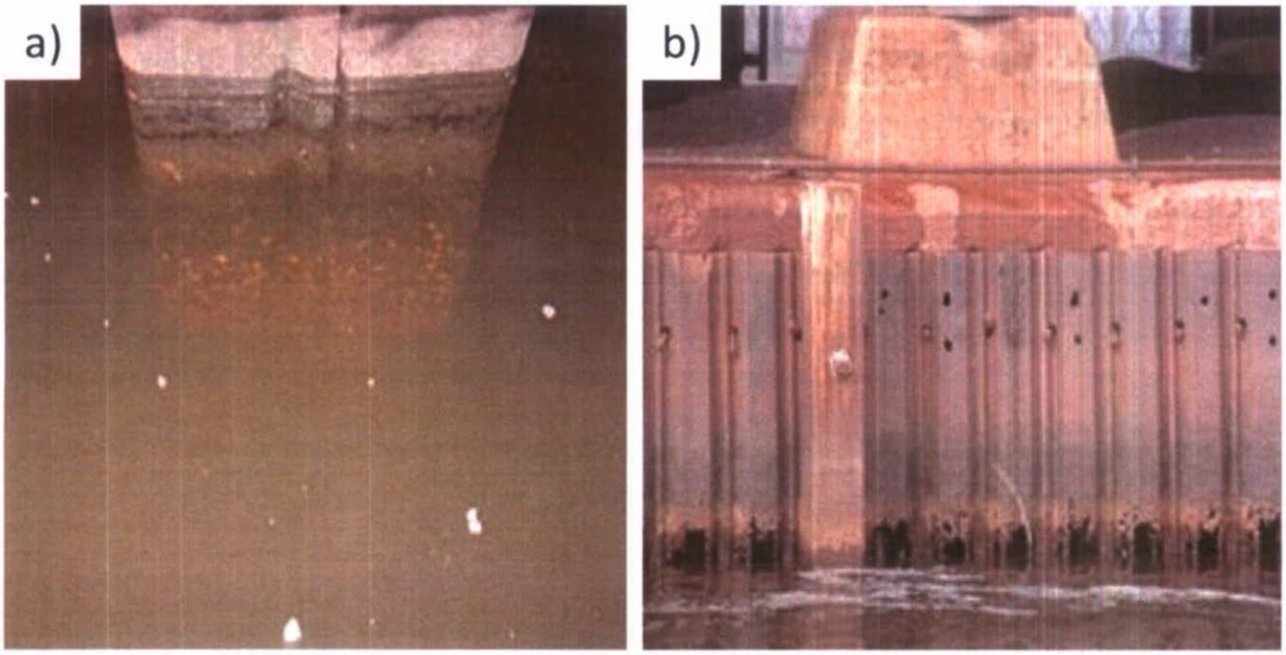

Figure 1. a) Top view of submerged DSH piling with visible orange tubercles. b) Side view of DSH piling with visible perforation at the water line. Photographs reproduced with permission from Gene Clark, Wisconsin Sea Grant Program.

Despite the identification of a corrosion mechanism that is consistent with the observations of localized corrosion in DSH, the environmental parameters that control the rate of penetration have not been identified. One of the remaining challenges is development of a method for making lifetime predictions for sections of new and existing untreated piling. The following is a comparison of data from DSH for three independent techniques traditionally used to evaluate corrosion loss and rates.

METHODS AND MATERIALS

Duluth Seaway Port Authority and the U.S. Army Corps of Engineers, Detroit District developed a method for exposing carbon steel coupons in a frame attached to existing piling. The standard coupon was 0.9525 cm thick A328 (0.035% max P, 0.04% max S and 0.20 % min Cu) cold rolled sheet pile cut to an average size of 19.3 x 11.6 cm and sand blasted to SP5 white metal blast cleaning specification.[10] Prior to exposure, the steel sheet pile structures were washed with a 4000-psi pressure washer to remove marine growth and any existing corrosion.[11] Sample trays were welded to the clean steel structures (AMI Consulting Engineers, Duluth, MN) using underwater welding techniques as described in

American Welding Society specification D3.6[12] using Broco® (Rancho Cucamonga, CA, USA) E70XX welding rods. Trays were installed with the top of the tray at 1 m below the Lake Superior International Great Lakes Datum water level.[13] Divers collected coupons from within the DSH and upstream in the St. Louis River at Oliver Bridge (Figure 2). At the time of collection, coupons were placed into Lucite® boxes with water from the collection site and shipped to the Naval Research Laboratory, Stennis Space Center, MS. Each coupon was removed from its Lucite® box and imaged using a Nikon S-700 digital camera. Procedures for examining tubercles have been described elsewhere.[9] Coupons were weighed to the nearest tenth of a gram before exposure and after acid-cleaning. Weight loss was corrected by subtracting weight loss of an unexposed coupon after acid-cleaning. Coupons were cleaned according to ASTM G1-03[14] by washing with a solution of hydrochloric acid and distilled water (1:1) with 3.5g L^{-1} of hexamethylene-tetramine. Coupons were digitally imaged after cleaning. Pit depths were measured in five locations on each coupon surface with a Microphotonics Nanovea PS50 non-contact optical profiler (profilometer) with a 3.5 mm optical laser pen and averaged. Linear polarization resistance (LPR) measurements[15] were made on September 7 and November 28, 2006. The techniques and data have been reported[16] where the average LPR-derived corrosion rate was multiplied by 7.5 to approximate pitting rate. Divers measured pit penetration in pilings using handheld instruments in 2006. Those data have been converted to $\mu m\ y^{-1}$ based on the reported ages of the pilings.

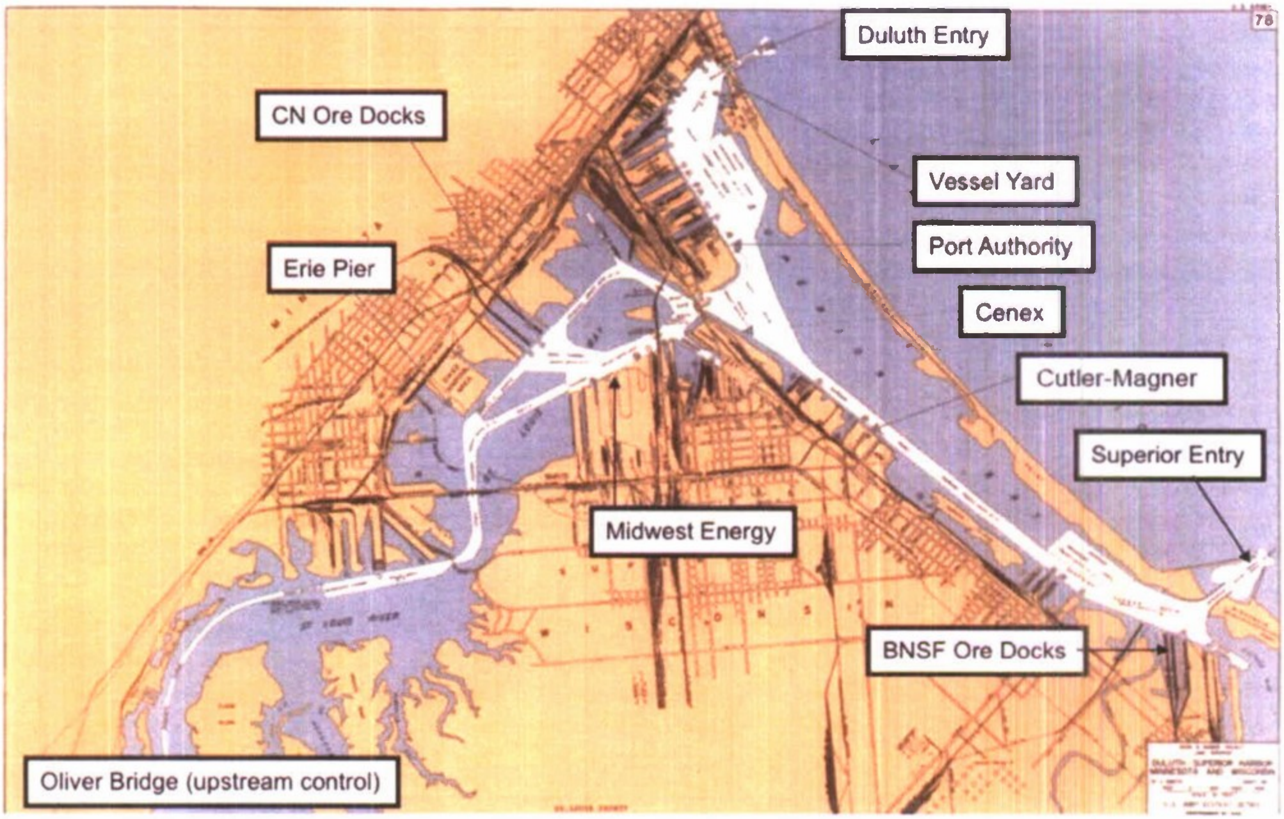

Figure 2. Map of Duluth Superior Harbor, MN and WI.

RESULTS AND DISCUSSION

Measured pit depth and weight loss are reported in Table 1. Corrosion rates ($\mu m\ y^{-1}$) calculated from those data were compiled by location for each exposure year (Table 2).

Table 1. Compilation of Measured Corrosion Data by Location

Location	Average Pit Depth (µm)			Weight loss (g)		
	10 mos.	Year 2	Year 3	10 mos.	Year 2	Year 3
Oliver Bridge	445.8	469.5		16.6	42.1	
Hallett 7 Dock				17.7	38.0	
Hallett 5 Dock				21.4	53.5	66.3
Midwest Energy Dock	393.6		668.4	20.9	44.5	59.5
DSPA Berth 4			738.2	24.0	53.6	76.7
Cutler Magner	387.1	610.6	787.8	28.0	61.5	80.3

Pit depth, a measure of localized corrosion in the 3-year coupons examined in this study, ranged between 668 to 788 µm, 5-6% of the total thickness of the coupons. Pit depth varied with location and increase in pit depth was not linear over the 3-year exposure. During the first year exposure average pit depths varied with location from 387 to 446 µm. The increase in pit depth in years two and three never approximated the pit growth during the first year exposure and judging from the samples collected at Cutler Magner, the penetration rate decreased each year over the three-year period of examination.

Weight loss, a measure of general corrosion, for coupons exposed in DSH was consistently 20-30 gm y^{-1} over the three-year period. Weight loss remained remarkably constant with an approximate 1% weight loss per year. The highest weight loss was measured at Cutler-Magner after the first year exposure. Sontheimer et al.[17] found that corrosion of iron pipes occurred quickly during the first few years after placement into a drinking water distribution system and then slowed. However, the decrease in corrosion rate over time in the drinking water distribution system was influenced by the formation of an intact scale layer, a situation that does not apply to the ice-scoured pilings in DSH.

Penetration rates (LPR x 7.5) measured on September 7 and November 28, 2006[16] are included in Table 2. Differences in data collected at the two different times demonstrate the influence of temperature on the measurements. The September measurements were taken at most sunlight and highest water temperature readings. A correlation between water conductivity and corrosion rates (measured by LPR) was also reported.[16] Despite these correlations there are no obvious correction factors that can be used to account for these influences.

Table 2. Compilation of Penetration Rate Data by Location in $\mu m\ y^{-1}$.

Coupon Data							Piling Pit Depth	CS Electrodes Sept. '06	CS Electrodes Nov. '06
Location	Pit depth			Weight loss				LPR x 7.5	LPR x 7.5
	Year 1	Year 2	Year 3	Year 1	Year 2	Year 3			
Oliver Bridge	535.0	234.8		51.1	54.1			1019.8	122.9
Hallett 7 Dock				54.6	48.9			1016.7	228.8
Hallett 5 Dock				66.0	68.7	55.3	183.4	1211.0	482.5
Midwest Energy Dock	472.0		222.8	64.0	57.2	49.6	125.7	1160.9	446.2
DSPA Berth 4			246.1	74.1	68.9	63.9	68.6	745.8	405.7
USACOE Duluth Entry								390.9	167.5
Cutler Magner	462.3	305.3	262.6	86.4	79.0	66.9	87.4	868.6	332.1

The three methods used to predict penetration rates in carbon steel at DSH measure different parameters. Profilometry provides an accurate measure of pit depth and volume. Weight loss is a direct measure of material loss and is appropriate for measuring/predicting general corrosion. When attack is uniform, however, as indicated in Table 2, weight loss cannot be used to predict penetration rates. Both weight loss measurements and profilometry require that a sample be exposed for a meaningful period of time, removed and examined in a laboratory. The data in Table 2 indicate that a one-year exposure may be too brief for an accurate lifetime prediction of carbon steel exposed in DSH. LPR is a method used to assess corrosiveness of an environment with respect to a metal. Thus, for example, LPR data can be used to compare corrosivity at different exposure sites. Since LPR determines instantaneous corrosion rates, it would be necessary to make repeated measurements over several years to determine if there is correlation of the LPR data and that observed on coupons over an equivalent time period. It is common practice to multiply LPR average corrosion rates by a factor of 5, 10 or 20 to determine the pitting or perforation rate. In this study, the average LPR-derived corrosion rate was multiplied by 7.5 to obtain a "...reasonable approximation of the pitting rate."[16]

While none of the techniques accurately predicts the precise penetration rate that was measured for the pilings, both methodologies (coupons and LPR) provide insight into the worst-case corrosion rates expected. Using LPR as an indicator of corrosivity, one would predict the deepest pitting at Midwest Energy and Hallett 5 Dock and those are the locations where divers measured the deepest pits in the pilings. The predicted rates based on August measurements are off by an order of magnitude. The penetration rates based on pit depths over 3 years overestimated the actual penetration rate by 2-3 fold. For the most part, weight loss measurements underestimated the penetration rate. The uniformity of weight loss measurements with time may indicate that weight loss is determined by ice abrasion. Rates of penetration in this case are attributed to a specific environment created by IOB, but the rate is not controlled by microbial activity. Penetration depends on chemical reactions – deposition of copper and galvanic corrosion.

CONCLUSIONS

Data in Tables 1 and 2 can be used to conclude the following. 1) There are no obvious relationships between the predicted rates, e.g. MPY calculated from weight loss is not directly related to MPY calculated from pit depth. 2) Corrosion rate is not linear as indicated by pit depth measurements. Localized corrosion in the first year exposure is more aggressive than in subsequent years. 3) Pit depth varied among the locations. The corrosion rate calculated from weight loss remained remarkably constant at all exposure sites over 3 years. 4) LPR measurements are influenced by temperature. In the absence of a better understanding of the relationship between water chemistry and tubercle formation and tubercles and corrosion, there are no scientific reasons to expect that the penetration rate will remain linear over decades.

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